Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supplementary Information

Interfacial acidity in ligand-modified ruthenium nanoparticles boosts the performance for the continuous hydrogenation of levulinic acid to gamma-valerolactone

Davide Albani,[a] Qiang Li,[b] Gianvito Vilé,[a] Sharon Mitchell,[a] Neyvis Almora-Barrios,[b] Peter T. Witte,[c]
Núria López,[b,]* Javier Pérez-Ramírez[a,]*

[a]*Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, CH-8093 Zurich, Switzerland. E-mail: jpr@chem.ethz.ch.*

[b]*Institute of Chemical Research of Catalonia (ICIQ) and Barcelona Institute of Technology (BIST), Av. Països Catalans 16, 43007 Tarragona, Spain. E-mail: nlopez@iciq.es.*

[c]*BASF Nederland BV, Strijkviertel 67, 3454PK De Meern, The Netherlands.*

Table of contents

1. Additional characterisation of the catalysts

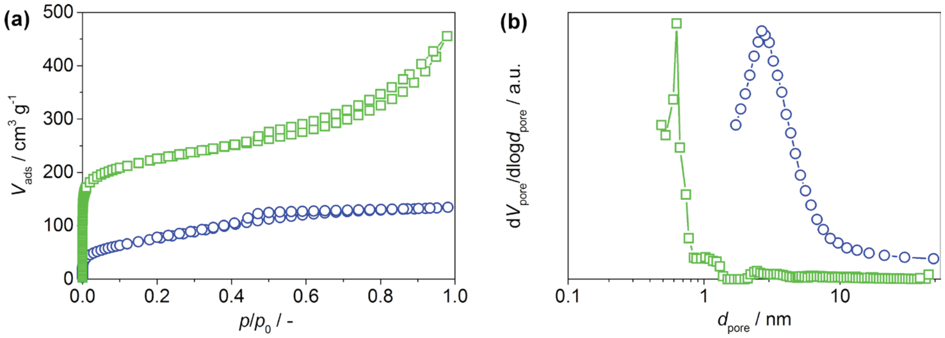


Fig. S1. N_2 adsorption and desorption isotherms (left) and relative pore size distribution (right) of Ru-HHDMA/$TiSi_2O_6$ (blue) and Ru/C (green).

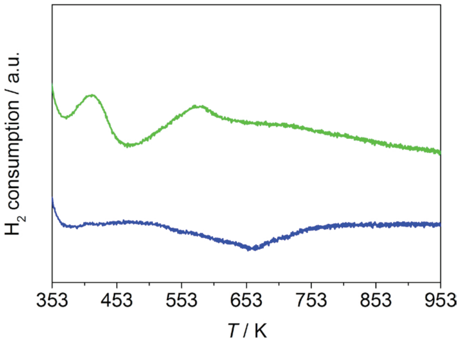


Fig. S2. H_2-temperature programmed reduction profiles of Ru-HHDMA/$TiSi_2O_6$ (blue) and Ru/C (green).

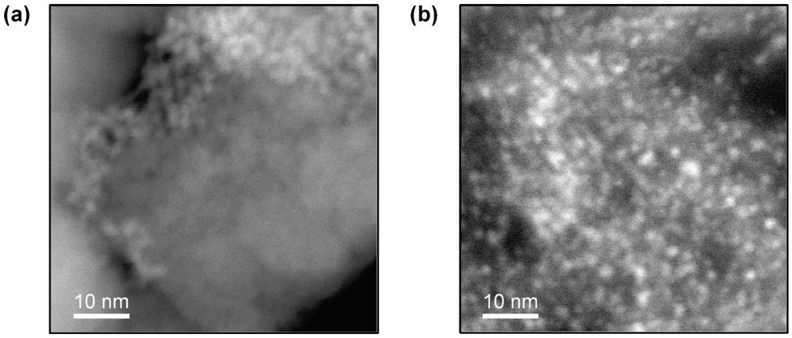


Fig. S3. Scanning transmission electron micrographs of Ru-HHDMA/$TiSi_2O_6$ (left) and Ru/C (right) after use in catalytic hydrogenation of levulinic acid.

2. Reaction mechanism

Table S1. Adsorption energies (in eV) on pure Ru(0001) surface.

Species	H	O	H_2O	LA[a]	GVL[a]	23-c[b]
E_{ads}	–0.68	–2.14	–0.52	–1.03 (–0.76)[c]	–1.24 (–0.80)[c]	–0.47

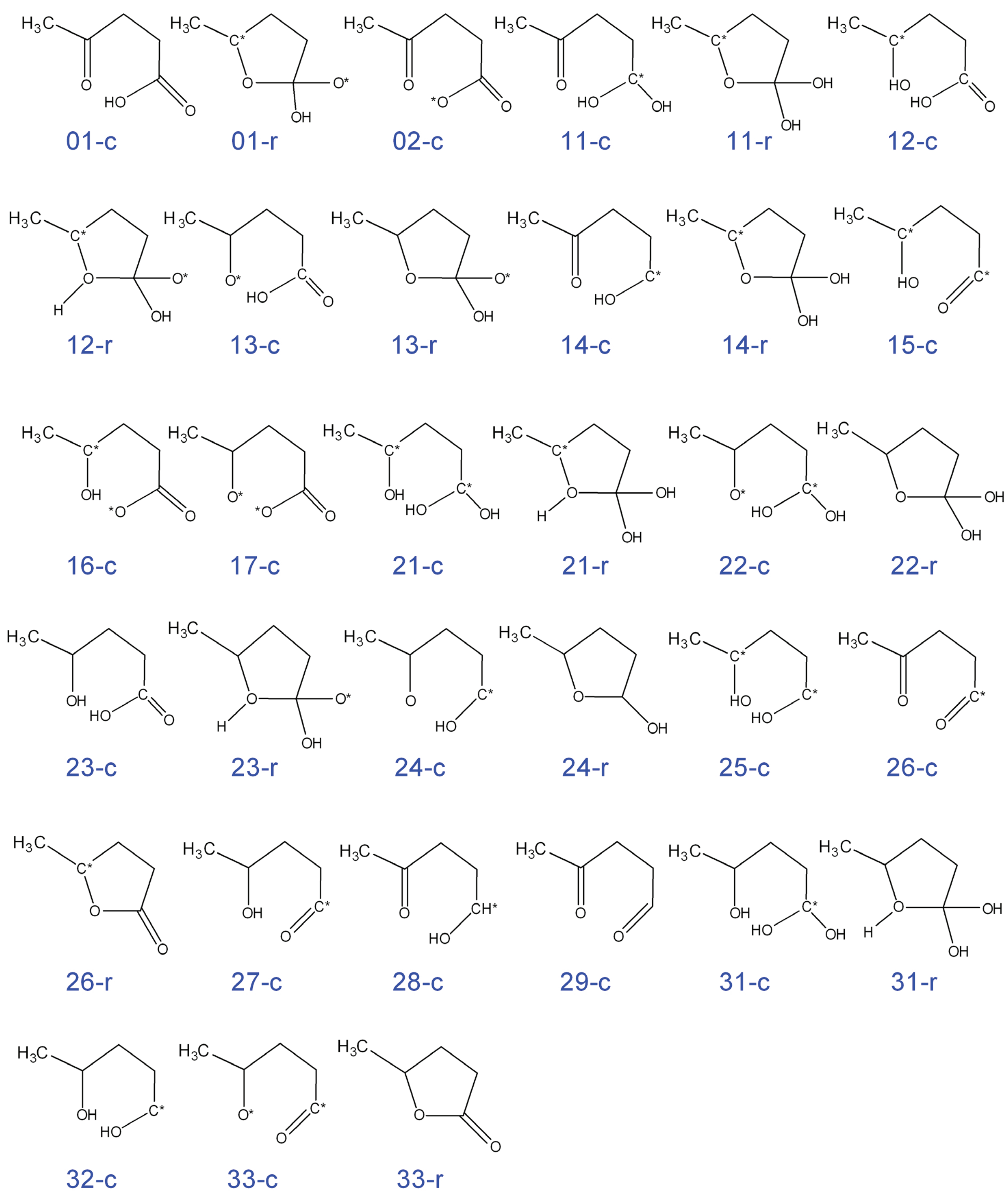
[a]The solvation energies for LA and GVL were calculated in the gas phase, and are of –0.68 and –0.34 eV, respectively; [b]23-c refers to 4-hydroxypentanoic acid, see Fig. S4; [c]$E_{\text{ads-sol}} = E_{\text{slab + adsorbate}} - E_{\text{slab}} - E_{\text{adsorbate,gas}}$, the energy values have been calculated with the VASP-MGCM methodology (Vienna ab initio Simulation Package-Multigrid Continuum Model).

Table S2. Reaction energies, ΔE, and barriers for the direct and inverse reactions, $E_{a,d}$ and $E_{a,i}$ (in eV) of the elementary steps considered in this study.

Reaction[a]	IS	FS	ΔE	$E_{a,d}$	$E_{a,i}$
RC	01-c	01-r	0.10	1.16	1.06
HT	01-r	01-r	0.00	1.95	1.95
O^1+H	01-c	11-c	0.46	1.35	0.89
O^1+H	01-r	11-r	0.90	1.68	0.78
O^2+H	01-c	12-c	0.49	1.37	0.88
C^2+H	01-c	13-c	0.19	1.17	0.98
C^2+H	01-r	13-r	–0.09	1.05	1.14
C-OH	01-c	26-c	–0.33	0.46	0.80
O^1+H	02-c	01-c	0.69	1.34	0.65
O^2+H	02-c	16-c	1.13	1.33	0.20
C^2+H	02-c	17-c	–0.54	0.57	1.10
C-O	02-c	26-c	0.38	1.56	1.19
RC	11-c	11-r	0.55	1.11	0.59
HT	11-c	12-c	0.03	0.26	0.22
C-OH	11-c	14-c	–0.02	1.15	1.18
C-OH	11-r	14-r	–0.46	0.81	1.27
O^2+H	11-c	21-c	0.57	1.37	0.80
C^2+H	11-c	22-c	0.49	1.27	0.78
C^2+H	11-r	22-r	–0.06	1.06	1.11
HT	12-c	11-c	–0.03	0.22	0.26
RC	12-c	11-r	0.51	1.37	0.86
HT	12-c	12-c	0.00	0.49	0.49
C-OH	12-c	15-c	–0.40	0.35	0.75
O^1+H	12-c	21-c	0.54	1.53	0.99
C^2+H	12-c	23-c	–0.28	1.13	1.41
RC	13-c	13-r	–0.18	0.34	0.52
HT	13-r	13-r	0.000	1.54	1.54
O-H	13-c	17-c	–1.42	1.37	2.79
O^1+H	13-c	22-c	0.75	1.64	0.89

O^1+H	13-r	22-r	0.94	1.47	0.53
O^2+H	13-c	23-c	0.02	1.44	1.41
C-OH	13-c	33-c	–0.65	0.21	0.86
RC	14-c	14-r	0.11	0.44	0.34
C^2+H	14-c	24-c	–0.05	1.26	1.34
C^2+H	14-r	24-r	0.10	0.90	0.80
O^2+H	14-c	25-c	0.48	1.57	1.08
O-H	14-c	26-c	–0.77	0.90	1.67
O-H	14-r	26-r	–0.47	0.77	1.23
C^1+H	14-c	28-c	0.65	0.57	–0.08
O-H	15-c	26-c	–0.42	0.73	1.15
Rotation	16-c	01-c	–0.44	0.10	0.54
O^1+H	17-c	13-c	1.42	2.50	1.08
C-O	17-c	33-c	0.78	1.39	0.60
C-OH	21-c	25-c	–0.11	0.72	0.83
C^2+H	21-c	31-c	–0.11	1.19	1.29
RC	22-c	22-r	0.01	0.81	0.81
HT	22-c	23-c	–0.73	0.27	1.00
C-OH	22-c	24-c	–0.56	0.55	1.12
C-OH	22-r	24-r	–0.30	1.16	1.47
O^2+H	22-c	31-c	–0.02	1.15	1.17
RC	23-c	22-r	0.73	1.93	1.20
C-OH	23-c	24-c	0.17	1.28	1.12
C-OH	23-c	27-c	–0.16	0.54	0.69
O^1+H	23-c	31-c	0.71	1.90	1.19
RC	24-c	24-r	0.26	0.70	0.44
HT	24-c	27-c	–0.32	1.32	1.64
O-H	24-c	33-c	–0.80	0.66	1.50
O-H	24-r	33-r	–0.52	0.85	1.36
C^2+H	25-c	32-c	0.36	0.99	0.63
O^1+H	26-c	14-c	0.77	1.67	0.90
O^2+H	26-c	15-c	0.42	1.15	0.73
RC	26-c	26-r	0.41	0.44	0.04
C^1+H	26-c	29-c	0.27	0.66	0.39
C^2+H	26-c	33-c	–0.12	0.80	0.92
C^2+H	26-r	33-r	0.05	0.87	0.82
C-OH	31-c	32-c	0.36	0.72	0.36
O^2+H	33-c	27-c	0.52	1.24	0.72
RC	33-c	33-r	0.59	0.68	0.09

[a] IS and FS correspond to the initial and final states (see **Fig. S4** for the structure codes); RC and HT stand for ring closing and hydrogen transfer reaction, respectively. O^n+H and C^n+H refer to protonation of the oxygen atom, and to the hydrogenation of the carbon atom, respectively. *n* can be 1 or 2, where 1 indicates that atom involved in the chemical transformation belongs to the carboxylic moiety, whereas, 2 to the ketone one. C-OH stands for the cleavage reaction.


01-c 01-r 02-c 11-c 11-r 12-c

12-r 13-c 13-r 14-c 14-r 15-c

16-c 17-c 21-c 21-r 22-c 22-r

23-c 23-r 24-c 24-r 25-c 26-c

26-r 27-c 28-c 29-c 31-c 31-r

32-c 33-c 33-r

Fig. S4. Species considered in the reaction network of levulinic acid hydrogenation to γ-valerolactone over the Ru(0001) surface.

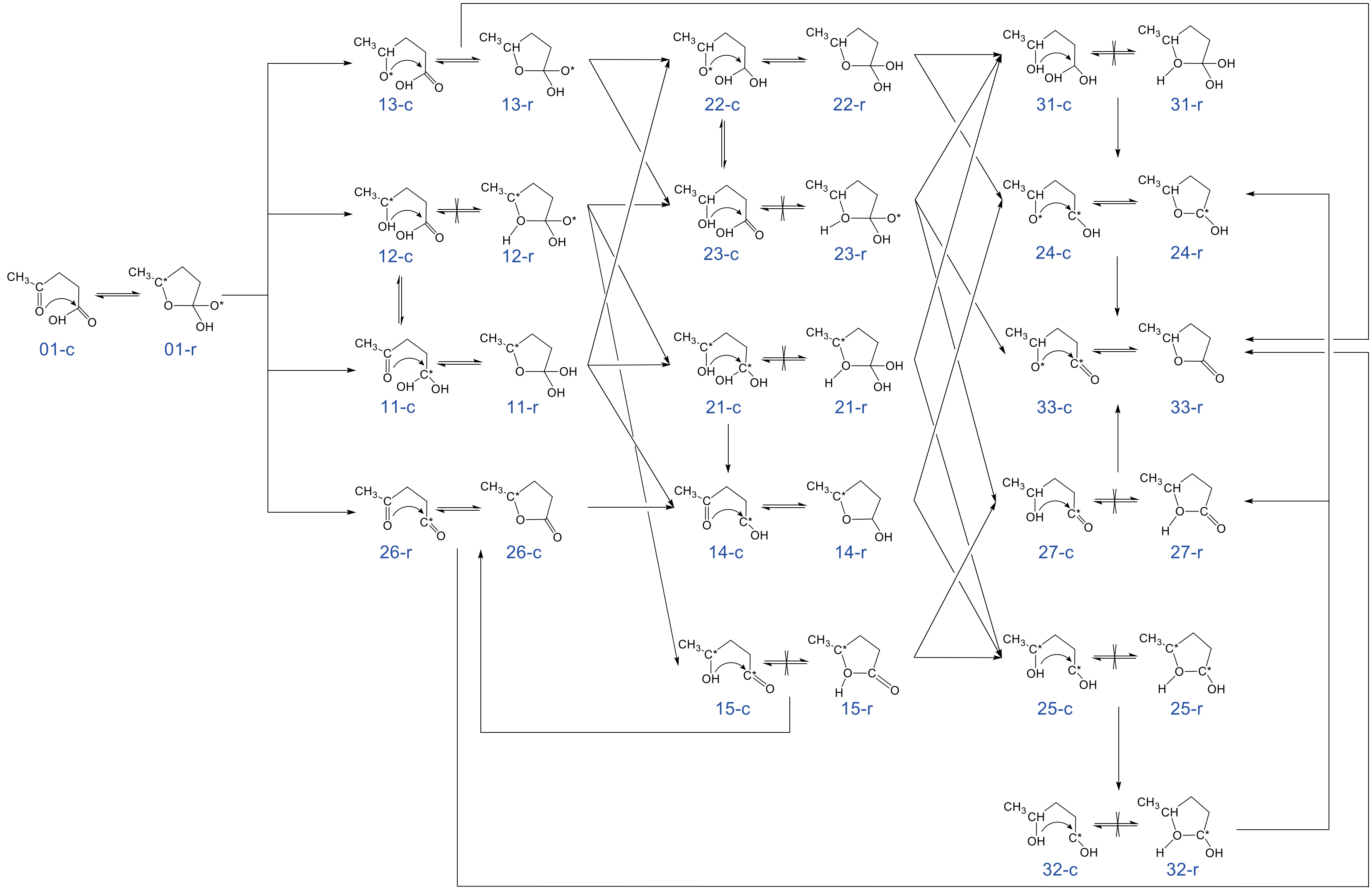


Fig. S5. Complete reaction network starting from levulinic acid (01-c) to γ-valerolactone (33-r).

3. Calculated properties of Ru(0001) and Ru(0001)+HHDMA

3.1. Oxidation properties

One $p(2\times2)$ unit cell (3 layers relaxed), and one covered with HHDMA molecules ($\theta_{\text{HHDMA}} = 0.25$) were used to assess the oxidation propensity of ruthenium. The calculations were performed with 5×5×1 *k*-points. In order to get a $p(4\times4)$ unit cell from the starting ones, the systems were multiplied by 2 in both *x* and *y* directions the *k*-point sampling was reduced accordingly.

Table S3. Average and differential adsorption energies (in eV) of O on Ru(0001) and Ru(0001)+HHDMA.

Location	O number	Ru(0001)		O number	Ru(0001)+HHDMA	
		E_{average}[a]	$E_{\text{differential}}$[b]		E_{average}	$E_{\text{differential}}$
1st layer	1	–3.319	–3.319			
	2	–2.832	–2.345			
	3	–2.539	–1.953	1	–2.353	–2.353
	4	–2.256	–1.407	2	–2.046	–1.740
2nd layer	5	–1.671	0.670	3	–1.206	0.475
	6	–1.419	–0.161	4	–1.140	–0.942
	7	–1.463	–1.725	5	–1.188	–1.380
	8	–1.545	–2.122	6	–1.205	–1.293

[a] $E_{\text{average}} = [E_{(\text{slab}+n\text{O})} - E_{(\text{slab})} - n\times E_{(\text{O2})}/2]/n$

[b] $E_{\text{differential}} = E_{(\text{slab}+n\text{O})} - E_{(\text{slab}+(n-1)\times\text{O})} - E(_{\text{O2}})/2$

The oxygen atoms used for the calculation are added as extra atoms, in principle they can come both from water and levulinic acid.

Table S3 shows that Ru(0001)+HHDMA can adsorb only two oxygen atoms in the first ruthenium layer. This is due to the presence of the orthophosphate group attached to the surface, resulting in a shielding effect towards oxidation.

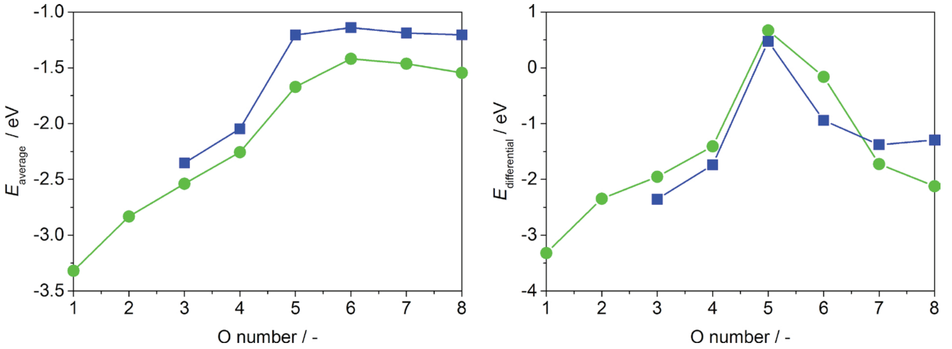


Fig. S6. Average (left) and differential (right) O adsorption energies *versus* O number of Ru-HHDMA/$TiSi_2O_6$ (blue) and Ru/C (green).

Moreover, we investigated if oxygen atoms were stable on the surface provided that H atoms are present. For O* + H* → OH*, the activation barrier and the reaction energy are (1.38 and 0.57 eV, respectively) on Ru(0001) and (1.22 and 0.20 eV, respectively) on Ru(0001)+HHDMA. The lower values encountered on Ru(0001)+HHDMA imply that O protonation is much easier, leading to the formation of a stable OH group. The latter hinders the formation of RuO_x species as less oxygen is available.

3.2. Acidity properties

Table S4. Adsorption energies for the carboxylates, E_{ads}, and reaction energies for protonation, ΔE, on Ru(0001)+HHDMA. Both energies are expressed in eV. Data plotted in **Fig. 11** of the main manuscript.

pK_a	E_{ads}	Reaction	ΔE
3.75	–1.25	$\mathrm{HCOO^- + H_3O^+ \rightarrow HCOOH + H_2O}$	0.47
4.75	–1.56	$\mathrm{CH_3COO^- + H_3O^+ \rightarrow CH_3COOH + H_2O}$	0.35
2.85	–1.11	$\mathrm{ClCH_2COO^- + H_3O^+ \rightarrow ClCH_2COOH + H_2O}$	0.53
1.29	–0.83	$\mathrm{Cl_2CHCOO^- + H_3O^+ \rightarrow Cl_2CHCOOH + H_2O}$	0.50
0.65	–0.53	$\mathrm{Cl_3CCOO^- + H_3O+ \rightarrow Cl_3CH_2COOH + H_2O}$	0.76

3.3. XPS shifts

Table S5. DFT-calculated binding energies shift (in eV) of 3*d* core level (corresponding to Fermi level) of Ru(0001) and Ru(0001)+HHDMA, as a function of the number of O atoms adsorbed.

Surface	Ru layer	Ru(0001)	Ru(0001)+HHDMA
		E_{shift}[a]	E_{shift}
Clean	1st	0.59	0.22
	2nd	0.00	–0.07
	3rd	0.00	0.03
1st layer covered	1st	–0.70	0.09
	2nd	0.08	0.03
	3rd	–0.12	–0.11
2nd layer covered	1st	–0.82	–0.54
	2nd	–0.06	–0.17
	3rd	–0.16	–0.26

[a] The third layer of Ru atoms in the clean surface was assumed to be representative of the bulk, and taken as reference for calculating the binding energy shifts. In the calculation of binding energies shift, three Ru layers have been considered. The first two layers for each system (Ru(0001) and Ru(0001)+HHDMA) have been covered with the maximum amount of O adsorbed per layer (see **Table S3**).